CERTIFICATE

I, Toshio NISHIZAWA, a citizen of JAPAN, residing at, 4-3-14, KUDAN-KITA, CHIYODA CITY, TOKYO, JAPAN hereby certify that I am conversant with the English and Japanese language, and I further certify that to the best of my knowledge and belief the foregoing is a true and correct English translation of the Japanese Patent Application No. JP 2004-192223, attached heteto.

Signed this 13th day of April, 2012

Toshio Nishizawa

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【Title of the document】Scope of claims

【claim 1】 A hollow structural needle crystal comprising fullerene molecules.

【claim 2】 A needle crystal as claimed in Claim 1, wherein the fullerene molecule is a C_{60}, C_{70} or higher order fullerene, metal-intercalating fullerene or fullerene derivative.

【claim 3】 A needle crystal as claimed in Claim 1 or 2, being denatured by heating or electron beam.

【claim 4】 A needle crystal as claimed in any one of Claims 1 to 3, being in a closed form or holed form.

【claim 5】 A method for preparing a hollow structural needle crystal comprising fullerene molecules, which comprises (1) a step in which a solution containing a first solvent dissolving fullerene therein is combined with a second solvent in which the solubility of fullerene is lower than in the above first solvent; (2) a step in which a liquid-liquid interface is formed between the above solution and the above second solvent; and (3) a step in which a carbon fine wire is precipitated on the above liquid-liquid interface.

【claim 6】 A method for preparing C_{60} needle crystal, C_{60} hollow structural needle crystal, C_{60} needle crystal containing platinum or C_{60} platinum derivative, or C_{60} hollow structural needle crystal containing platinum or C_{60} platinum derivative by a liquid-liquid interfacial precipitation method, which comprises adding an alcohol to an organic solution of C_{60} to which has been added C_{60} platinum derivative.

【claim 7】 A method for preparing C_{60} needle crystal, C_{60} hollow structural needle crystal, C_{60} needle crystal containing platinum or platinum derivative, or C_{60} hollow structural needle crystal containing platinum or C_{60} platinum

derivative by a liquid-liquid interfacial precipitation method from isopropyl alcohol and a saturated toluene solution of C_{60} to which has been added a C_{60} platinum derivative $((\eta^2\text{-}C_{60})Pt(PPh_3)_2)$.

【Title of the document】 Specification

【Title of the invention】 FULLERENE HOLLOW STRUCTURE NEEDLE CRYSTAL AND METHOD FOR PREPARATION THEREOF

【Field of the invention】

The present invention relates to fullerene-type carbon materials, particularly a needle crystal (fullerene shell capsule) comprising fullerene molecules and having hollow structure and a method for preparation thereof.

【Prior art and problems thereof】

Recently, fullerene fine wire (fullerene nanowhisker, fullerene nanofiber) has been widely noticed by domestic and foreign research institutes, non-governmental enterprises, and universities, among which a keen competitive race for development has become serious. Previously, the present inventors developed a method for preparing fullerene fine wire by means of a liquid-liquid interface precipitation method (Patent documents 1 and 2; non-patent document 1).

In order to obtain carbon fine wire comprising fullerene as a component, the method for preparing carbon fine wire comprises (1) a step in which a solution containing a first solvent dissolving fullerene therein is combined with a second solvent in which the solubility of fullerene is lower than in the above first solvent; (2) a step in which a liquid-liquid interface is formed between the above solution and the above second solvent; and (3) a step in which carbon fine wire is precipitated on the above liquid-liquid interface. The present inventors further have elucidated that irradiation of a visible light during the growth of fullerene fine wire greatly promotes the growth of the fine wire (non-patent document 2).

Further, Miyazawa, one of the present inventors, has discovered that thermal treatment of C_{60} nanotube affords a fullerene shell tube having amorphous carbon wall (non-patent document 3; Japanese Patent Application No. JP 2003-346117).

Patent document 1: JP-A-2003-1600

Patent document 2: USP-A-20020192143

Non-patent document 1: K. Miyazawa, Y. Kuwasaki, A. Obayashi and M. Kuwabara, "C60 nanowhiskers fromed by the liquid-liquid interfacial precipitation method", J.Mater, Res., 17(1)(2002) 83-88

Non-patent document 2: M. Tachibana, K. Kobayashi, T. Uchida, K. Kojima, M. Tanimura and K. Miyazawa, "Photo-assisted growth and polymerization of C60 nanaowhiskers", Chemical Physics Letter 374 (2003) 279-285

Non-patent document 3: Kun'ichi Miyazawa, Kogyo Zairyo, 52 (1)(2004) 24-25

【Disclosure of invention】

【Problems to be solved by the invention】

The purpose of the invention is to provide fullerenes having a feature in the new shape.

【Means for solving the problems】

The invention provides a capsule-like needle crystal (fullerene shell capsule) comprising fullerenes molecule such as C_{60} or C_{70} platinum derivative and having hollow structure. The present inventors previously developed a method for preparing fullerene fine wire by means of a liquid-liquid interfacial precipitation method; in this invention, this method is applied to allow the preparation of a capsule-like needle crystal (fullerene shell capsule) comprising C_{60} fullerene molecules and C_{60} platinum derivative.

The fullerene shell capsule is characterized by needle crystal comprising fullerene molecules such as C_{60} and having hollow structure. This fullerene shell capsule is a material that was first synthesized and discovered by means of the liquid-liquid interfacial precipitation method established by the present inventors as a method of synthesizing fullerene nanowhiskers at usual temperature. The hollow needle crystals comprising fullerene molecules have not yet been reported. The fullerene shell capsule is a new type of fullerenes, since there is no similar case. The fullerene shell capsule has utility as catalyst carrier material, raw material for plastic composite materials, storage material for gas such as hydrogen, catalyst for fuel cell, and the like.

That is, the invention provides (1) a hollow structural needle crystal comprising fullerene molecules.

In addition, the invention provides (2) the needle crystal as described in (1), wherein the fullerene molecule is a C_{60}, C_{70} or higher order fullerene, metal-intercalating fullerene or fullerene derivative.

In addition, the invention provides (3) the needle crystal as described in (1) or (2), being denatured by heating or electron beam.

The invention provides (4) the needle crystal as described in any of (1) to (3), being in a closed form or holed form.

The invention provides (5) a method for preparing a hollow structural needle crystal comprising fullerene molecules, which comprises (1) a step in which a solution containing a first solvent dissolving fullerene therein is combined with a second solvent in which the solubility of fullerene is lower than in the above first solvent; (2) a step in which a liquid-liquid interface is

formed between the above solution and the above second solvent; and (3) a step in which a carbon fine wire is precipitated on the above liquid-liquid interface.

In addition, the invention provides (6) a method for preparing C_{60} needle crystal, C_{60} hollow structural needle crystal, C_{60} needle crystal containing platinum or C_{60} platinum derivative, or C_{60} hollow structural needle crystal containing platinum or C_{60} platinum derivative by a liquid-liquid interfacial precipitation method, which comprises adding an alcohol to an organic solution of C_{60} to which has been added a C_{60} platinum derivative.

Further, the invention provides (7) a method for preparing C_{60} needle crystal, C_{60} hollow structural needle crystal, C_{60} needle crystal containing platinum or platinum derivative, or C_{60} hollow structural needle crystal containing platinum or C_{60} platinum derivative by a liquid-liquid interfacial precipitation method from isopropyl alcohol and a saturated toluene solution of C_{60} to which has been added a C_{60} platinum derivative ($(\eta^2\text{-}C_{60})Pt(PPh_3)_2$).

【Advantage of the invention】

There was no capsule-like fullerene characteristic in the shape in the invention. The fullerene shell capsule has a wide range of utility as catalyst supporting material, adsorbent, various gas preserving agent, light resin composite material, and the like. After use, the capsule may be decomposed to recover fullerene molecules for recycle use. By developing this technology, there is some possibility that hollow fullerene nano fiber (= "true fullerene shell tube") in which the tube wall is composed of fullerene molecule only may be prepared.

【Best mode for carrying out the invention】

The above liquid-liquid interfacial precipitation method developed by the present inventors is as follows.

The preparation of the carbon fine wire containing fullerene as a component comprises (1) a step in which a solution containing a first solvent dissolving fullerene therein is combined with a second solvent in which the solubility of fullerene is lower than in the above first solvent; (2) a step in which a liquid-liquid interface is formed between the above solution and the above second solvent; and (3) a step in which carbon fine wire is precipitated on the above liquid-liquid interface.

The preparation of fullerene shell capsule can be attained by controlling the rate of growth of crystal in the above liquid-liquid interface precipitation method, and the process can be carried out in a convenient way in a condition of usual temperature and atmospheric pressure using only an organic solution (2nd solution) to which has been added a platinum derivative. This process may be conducted under a usual white luminescent light or under a light of selected wavelength.

According to the invention, the fullerene shell capsule can be produced in a closed shape or in a holed shape. For example, a liquid-liquid interface is formed between isopropyl alcohol and a saturated C_{60} toluene solution, to which has been added several percent by weight of C_{60} Pt derivative ($(\eta^2\text{-}C_{60})Pt(PPh_3)_2$), in a glass bottle, which is allowed to stand at 10°C-25°C (desirously 20°C) for a day to 1 month or longer; thus, the precipitation method affords a hollow-structural needle crystal. The amount of $(\eta^2\text{-}C_{60})Pt(PPh_3)_2$ to be added is desirably 1-10 mass% for C_{60}.

The size of the resulting needle crystal is in the range of 10 nm to 100

micrometer in diameter and 10 nm to several micrometer in length.

The aspect ratio which is defined as the ratio of diameter to length, is 1 or more. Irradiation of electron beam to the resulting needle crystal makes platinum fine particle deposit in nanometer size, which can be dispersed. The needle crystal can be converted into amorphous structure by a secondary action such as vacuum thermal treatment at 600°C or higher or irradiation of electron beam with high energy of 100 keV or higher.

Further, the invention provides a guideline for obtaining a hollow fiber (true fullerene shell tube) comprising fullerene molecules. In addition, this method can be generally applied to higher order fullerenes of C_{70} or higher, metal-intercalating fullerenes and fullerene derivatives such as $C_{60}[C(COOC_2H_5)_2]$ in addition to the above-mentioned fullerenes.

【Example】

Example 1

<Method of Preparation>

A saturated toluene solution of C_{60} platinum derivative $(\eta^2\text{-}C_{60})Pt(PPh_3)_2$ was provided. $(\eta^2\text{-}C_{60})Pt(PPh_3)_2$ was purchased from Science Laboratories Co., Ltd. A special grade of toluene was used. The above saturated solution of toluene was put in a proper-sized clear glass bottle (preferred to use a bottle of 5mL - 20 mL volume) up to the half level, and the bottle was placed on a cooling plate and cooled to about 20°C or lower. Isopropyl alcohol (IPA; preferably special grade purity) cooled to about 20°C or lower was dropwise added slowly or poured along the wall of bottle with a pipette into the above glass bottle to form a liquid-liquid interface between the fullerene-toluene solution and IPA. A series of operations up to this step were

carried out under a usual white fluorescent light. The glass bottle in which a liquid-liquid interface was formed was allowed to stand at 20°C for a period of 13 to 55 days to grow needle crystals.

<Observation under a Transmission Electron Microscope>

Fig. 1 shows a TEM image of $(\eta^2\text{-}C_{60})Pt(PPh_3)_2$ needle crystal prepared by the liquid-liquid interfacial precipitation method using a saturated toluene solution of C_{60} platinum derivative $(\eta^2\text{-}C_{60})Pt(PPh_3)_2$ and isopropyl alcohol medium, and its HRTEM image and FFT (fast Fourier transform) figure. As clearly seen from the HRTEM image, the space between C_{60} cages in the $(\eta^2\text{-}C_{60})Pt(PPh_3)_2$ molecule is 0.98 nm, which is identical to the distance between the centers of C_{60} molecules in C_{60} nanowhisker. This indicates that the C_{60} molecule has to be arranged densely in the direction of the growth axis in order that the $(\eta^2\text{-}C_{60})Pt(PPh_3)_2$ needle crystal is capable of growing. This is an important guiding principle to form a long fiber of $(\eta^2\text{-}C_{60})Pt(PPh_3)_2$.

Example 2

<Method of Preparation>

A C_{60}-saturated toluene solution to which was added $(\eta^2\text{-}C_{60})Pt(PPh_3)_2$ was provided. $(\eta^2\text{-}C_{60})Pt(PPh_3)_2$ was purchased from Science Laboratories Co., Ltd. The purity of C_{60} was 99.5 % (MTR Co.), and a special grade of toluene was used. The amount of $(\eta^2\text{-}C_{60})Pt(PPh_3)_2$ to be added was 6 mass % for C_{60}. Otherwise, the growth of needle crystal was conducted in the same manner as in Example 1.

<Observation under a Transmission Electron Microscope>

Fig. 2 shows an example of a transmission electron microscopic (TEM)

image of C_{60} hollow needle crystal (fullerene shell capsule) generated in a C_{60}-6% (η^2-C_{60})Pt(PPh_3)$_2$ saturated toluene solution-IPA medium (JEM-4010, observed at 400kV). Fig. 3 shows an enlarged figure of the capsule portion of fullerene shell capsule. The existence of the hollow portion is apparent from the observation of a moire fringe.

In addition to the closed fullerene shell capsule, a holed fullerene shell capsule can also be prepared, as shown in the TEM photograph of Fig. 4. The holed fullerene shell capsule allows easy operation for the support of a functional group or catalyst. Fig. 5 shows the result of EDX analysis of the fullerene shell capsule shown in Fig. 3. It is found that the C_{60} platinum derivative (η^2-C_{60})Pt(PPh_3)$_2$ has been incorporated since platinum is detected. The peak of copper (Cu) is attributed to the TEM micro-grid backing.

Fig. 6 shows a high resolution TEM image (HRTEM) at the center in Fig. 3. This figure shows a state of C_{60} cages which are arranged at spaces of 1.0 nm. From Figs. 5 and 6, it is apparent that the materials shown in Figs. 2 and 3 are C_{60} hollow needle crystals containing (η^2-C_{60})Pt(PPh_3)$_2$. Fig. 7 shows a TEM image of (η^2-C_{60})Pt(PPh_3)$_2$-added C_{60} needle crystal with no cavity. From the TEM-EDX analysis of Fig. 8, it is confirmed that the C_{60} needle crystal of Fig. 7 contains the platinum derivative.

Example 3

The needle crystal obtained in Example 1 was irradiated with an electron beam at 400 keV energy and a beam density of about 200 pAcm^{-2}. Fig. 9 shows a TEM image of (η^2-C_{60})Pt(PPh_3)$_2$- added C_{60} needle crystal in an amorphous state. Fig. 10 shows an HRTEM image of platinum nano particle

generated in the needle crystal of Fig. 9, and a lattice image of the platinum particle (111) surface. Such a C_{60} needle crystal in which the platinum nano particles are dispersed is expected to be useful as a catalyst for fuel cell.

Example 4

<Method for preparation of a C_{60} nanotube (hollow fiber) and C_{60} needle crystal having a hollow portion>

Fullerene powder of a C_{60}-1 mol% $(\eta^2\text{-}C_{60})Pt(PPh_3)_2$ composition (C_{60}-2 mass % $(\eta^2\text{-}C_{60})Pt(PPh_3)_2$ composition)(MRT Co.) was dissolved in 5 mL of toluene by ultra-sonication to give a saturated solution. This fullerene-saturated toluene solution (10 mL) was placed in a clear glass bottle, to which was added an approximately the same volume of isopropyl alcohol (IPA) slowly with a pipette to form a liquid-liquid interface between the lower toluene solution and the upper IPA. The liquid was kept at 20°C or lower. The glass bottle was stored in a low temperature incubator at 20°C for 10 days.

<Observation under a Transmission Electron Microscope>

The deposit yielded in the glass bottle was placed on a carbon micro-grid and observed with a transmission electron microscope (JEM-4010, accelerating voltage 400 kV). Fig. 11 shows a C_{60} nanotube (C_{60}NT) of 340 nm in diameter, 46 ± 9 nm in wall thickness, and 5 μm or more of length. There are many nano-sized openings on the C_{60}NT wall; therefore, a variety of molecules can be incorporated in the tube; this indicates that the nanotube has a high specific surface area.

Fig. 12 shows a high resolution TEM image (HRTEM) of Fig. 11. As

shown in Fig. 12, this C_{60}NT can be represented by an exponent as a face-centered cubic crystal (fcc) of the lattice constant a= 1.36 ± 0.02 nm. It was found that the central space between the C_{60} molecules becomes narrow by about 4% in comparison with C_{60} molecule crystal (fcc, lattice constant a = 1.417 nm) at usual temperature and atmospheric pressure.

Fig. 13 shows a TEM image of C_{60}NT having a smaller aspect ratio. This is found to be crystalline, as shown in the electron diffraction pattern of C_{60}NT indicated by A in Fig. 13. Further, it is also found that there are many nano-sized openings on the C_{60}NT surface.

As shown in Fig. 14, a C_{60} tubular structure having a wedge-form end (a hollow wedge-form C_{60} needle crystal) was also prepared. As shown by an arrow mark in Fig. 14, moire stripes are observed, which indicate the surface layer being single crystal. It was also found that the surface of the hollow wedge-form C_{60} needle crystal has completely closed structure.

Fig. 15 shows a C_{60} needle crystal of which only one end has closed structure. As shown by an arrow mark C in the needle crystal A, it is found that it is a single crystal of which the surface shell structure is C_{60} since moire stripes are observed. B is a C_{60} needle crystal having a small aspect ratio of about 2; from its form, a growth mechanism is proposed that the growth of the hollow-structural C_{60} crystal proceeds through first formation of shell structure and subsequent filling of the inside.

Fig. 16 supports the above-mentioned growth mechanism. Fig. 16 is an example of the preparation of a C_{60} needle crystal having a hollow portion A. The hollow portion A in the C_{60} needle crystal is considered to be formed because the needle crystalline shell structure with closed structure grows at

the terminal portion and cannot fill up completely the inside of crystal. The linear contrast B indicating that the clearer low-dense structure is formed along the growth axis suggests that the cavity has been formed during growth.

【Brief description of the drawings】

Fig. 1 shows a TEM image (a) and an HRTEM image (b) of $(\eta^2\text{-}C_{60})Pt(PPh_3)_2$ needle crystal prepared from a saturated toluene solution of $(\eta^2\text{-}C_{60})Pt(PPh_3)_2$ and an isopropyl alcohol medium by a liquid-liquid interfacial precipitation method. The unit cell is indicated by a rectangle.

Fig. 2 shows a TEM image (400kV) of fullerene shell capsule.

Fig. 3 shows a TEM image of C_{60} fullerene shell capsule.

Fig. 4 shows a holed TEM image of fullerene shell capsule.

Fig. 5 shows an EDX analysis of C_{60} fullerene shell capsule (Fig. 3) by a transmission electron microscope.

Fig. 6 shows an HRTEM image for a fullerene shell capsule in Fig. 3.

Fig. 7 shows a TEM image of C_{60} needle crystal to which has been added $(\eta^2\text{-}C_{60})Pt(PPh_3)_2$.

Fig. 8 shows a TEM-EDX analysis of C_{60} needle crystal (Fig. 7) containing C_{60} Pt derivative $((\eta^2\text{-}C_{60})Pt(PPh_3)_2)$.

Fig. 9 shows a TEM image of C_{60} needle crystal containing $(\eta^2\text{-}C_{60})Pt(PPh_3)_2$ which is amorphous by irradiation of electron beam.

Fig. 10 shows (a) platinum nano particles (particle size = 3.2 ± 0.8 nm) generated by irradiating a $(\eta^2\text{-}C_{60})Pt(PPh_3)_2$-added C_{60} needle crystal with electron beam; and (b) an HRTEM image of the platinum nano particle.

Fig. 11 shows a TEM image of C_{60} nanotube.

Fig. 12 shows an HRTEM image of C_{60} nanotube of Fig. 11.

Fig. 13 shows a TEM image of C_{60} nanotube closing at the both ends.

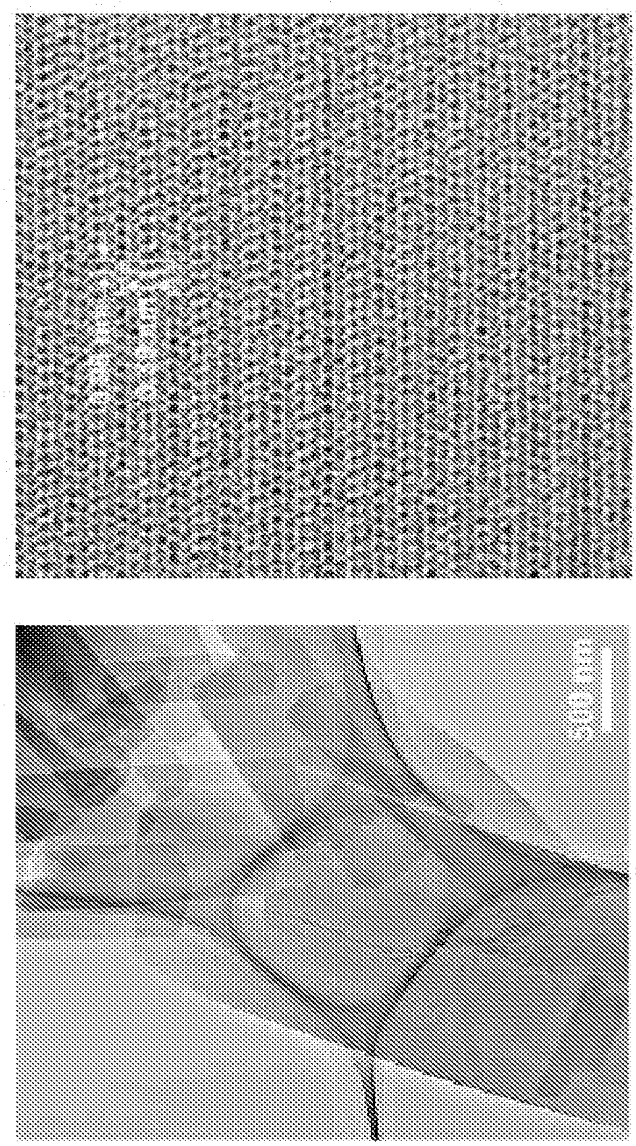
Fig. 14 shows a TEM image of a hollow wedge-form C_{60} needle crystal having closed shell structure.

Fig. 15 shows a TEM image of C_{60} nanotube (A, B) closing only at one end.

Fig. 16 shows a TEM image of C_{60} needle crystal having a hollow portion A.

【Title of the document】Drawings

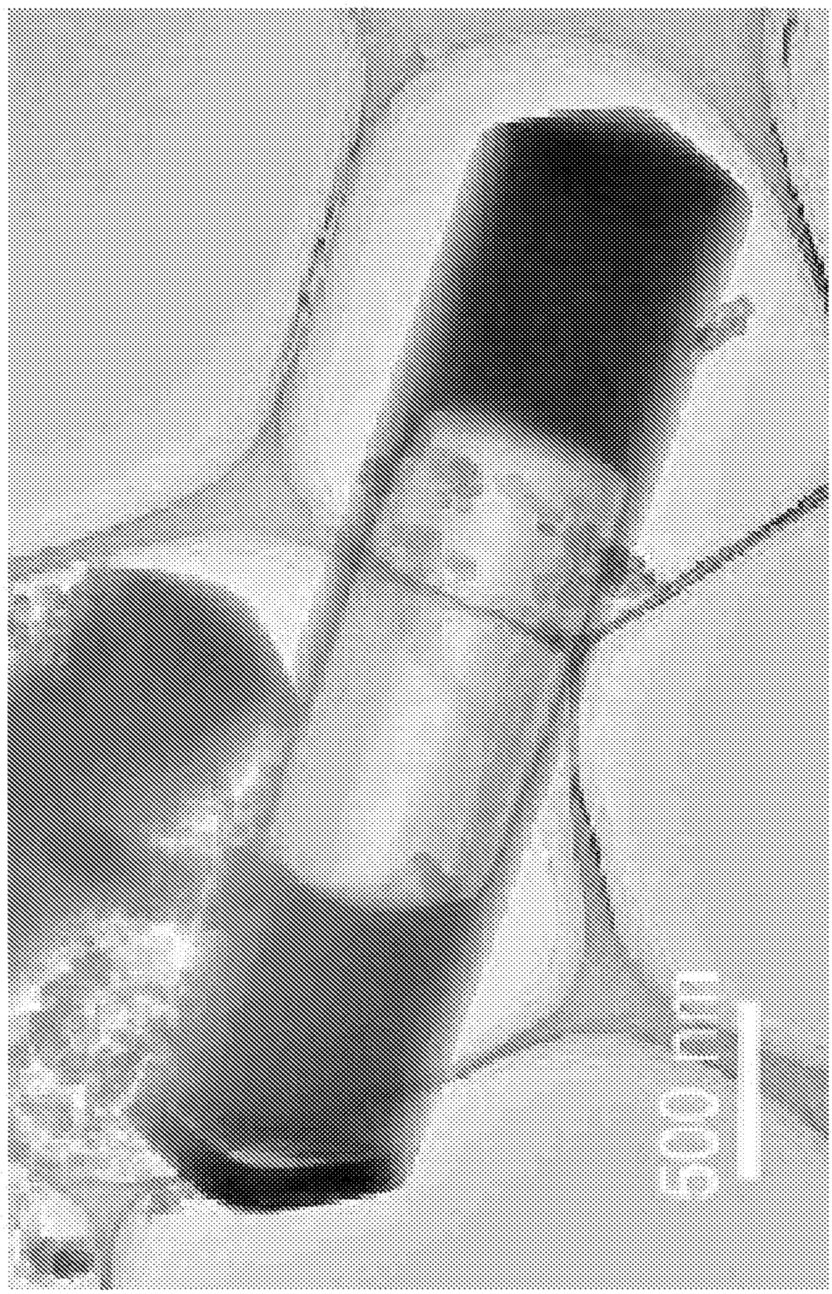
【Fig.1】



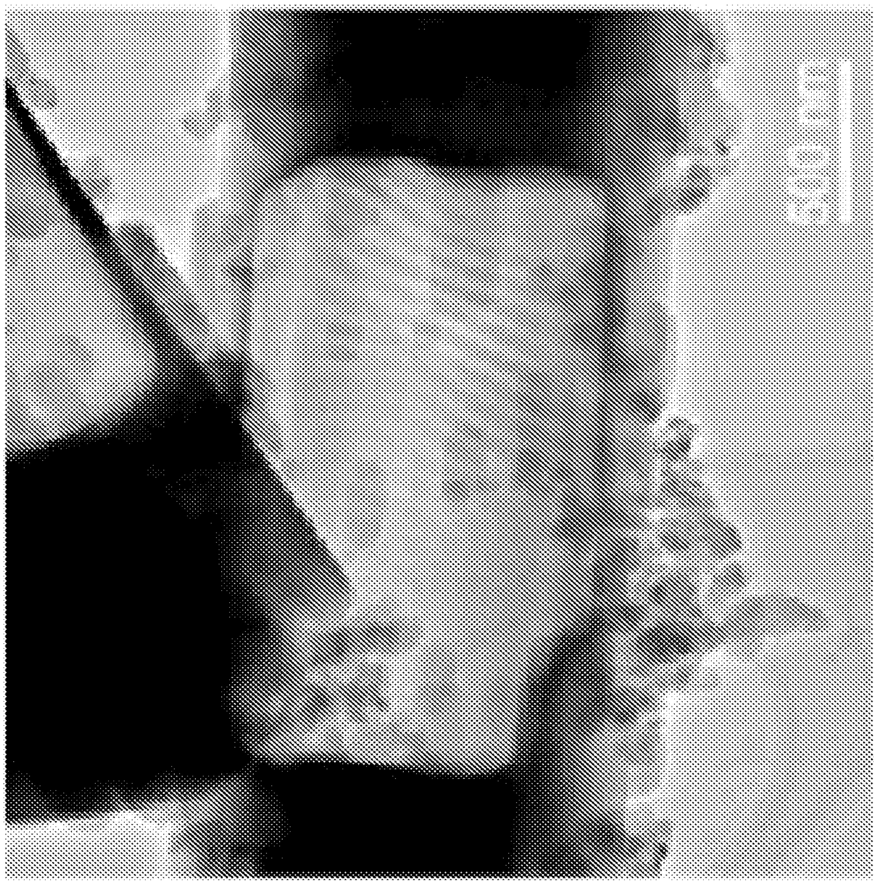
(b)

(a)

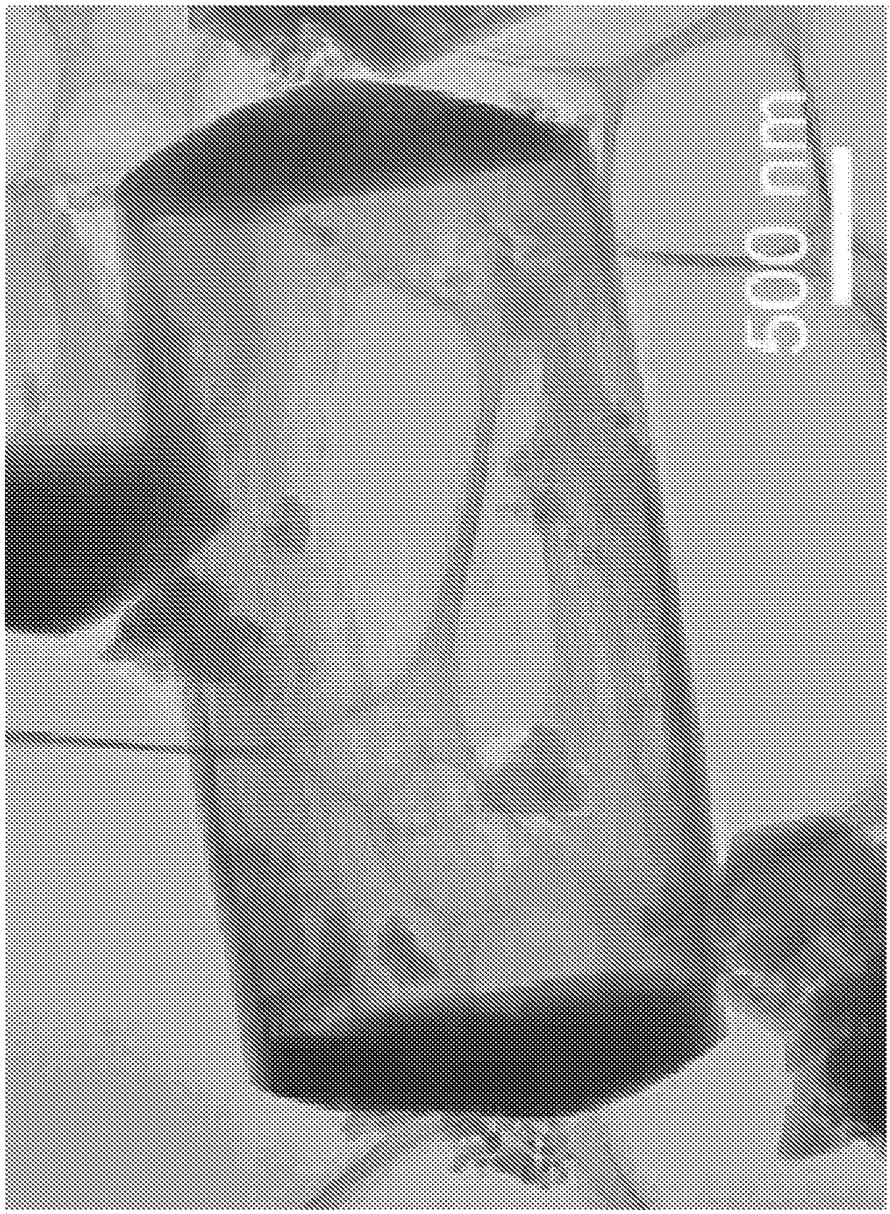
【Fig.2】



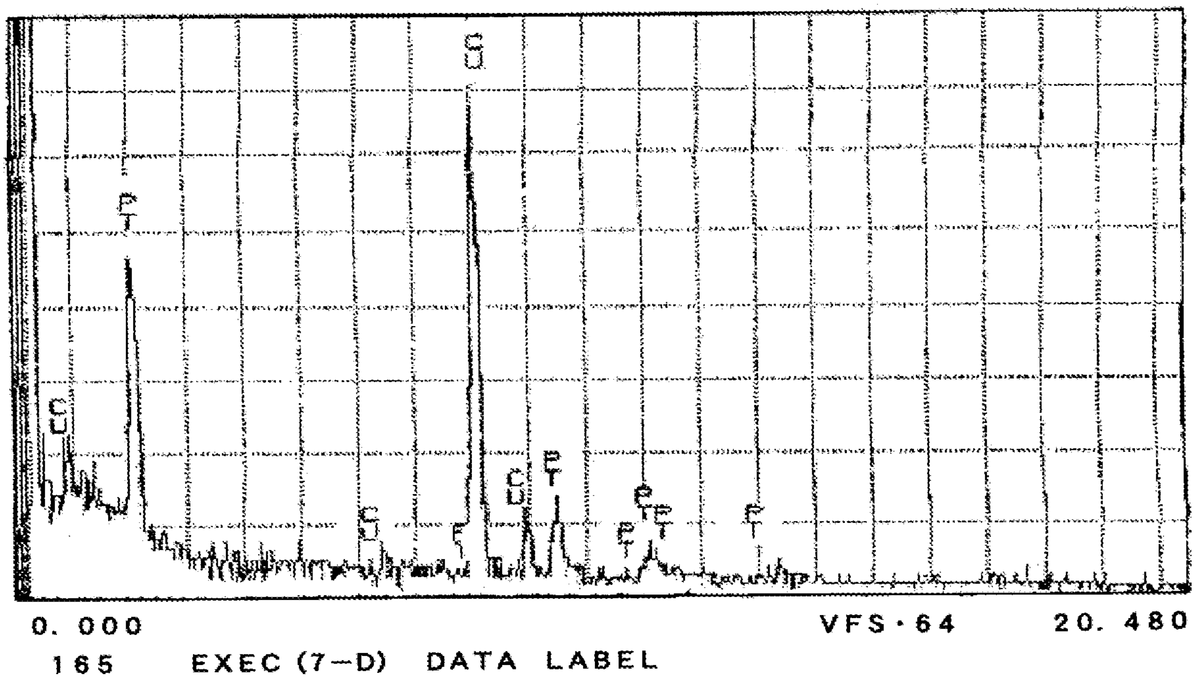
【Fig.3】



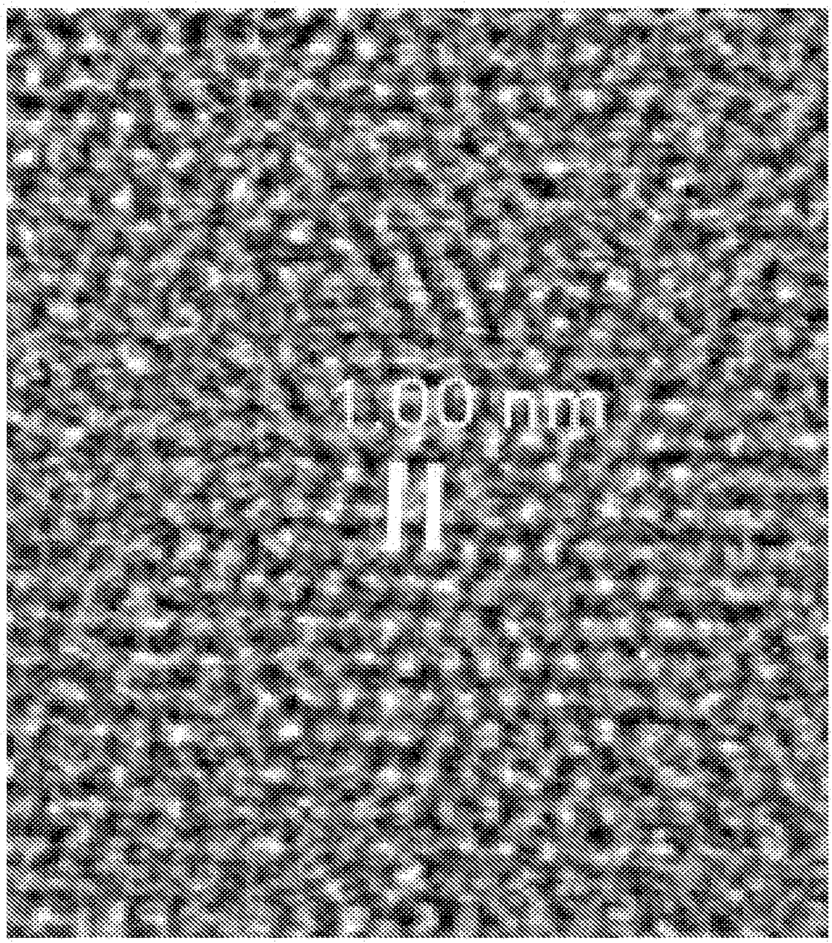
【Fig.4】



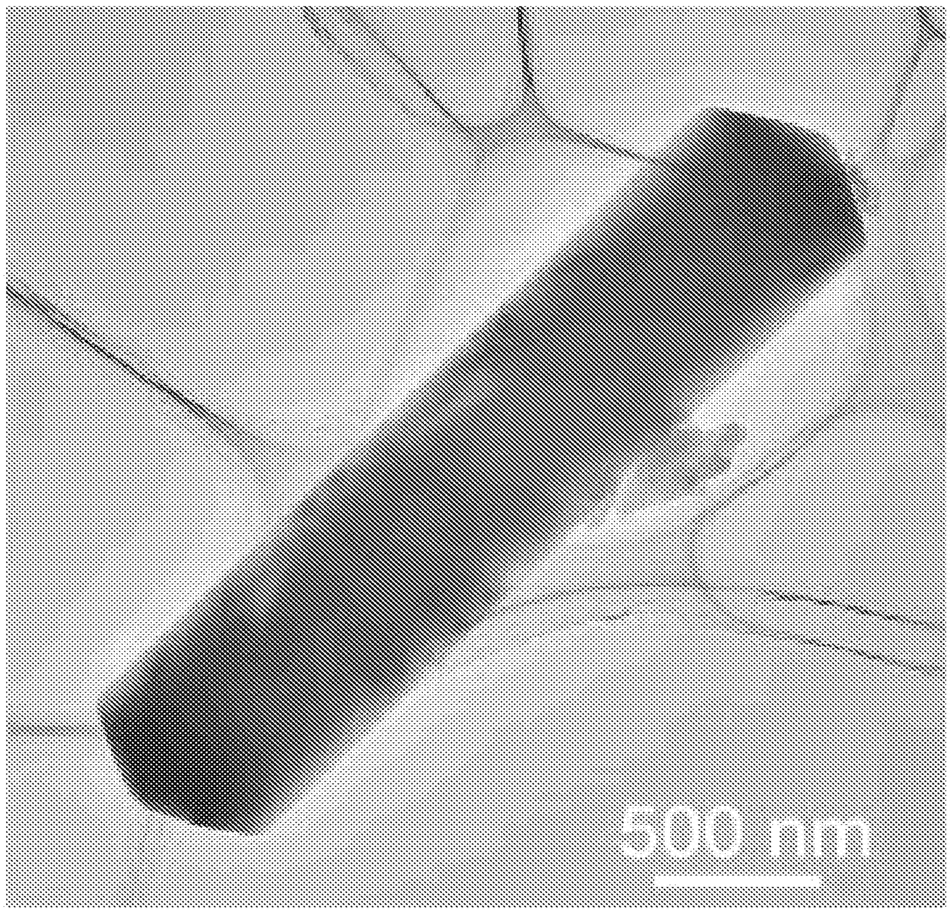
【Fig.5】



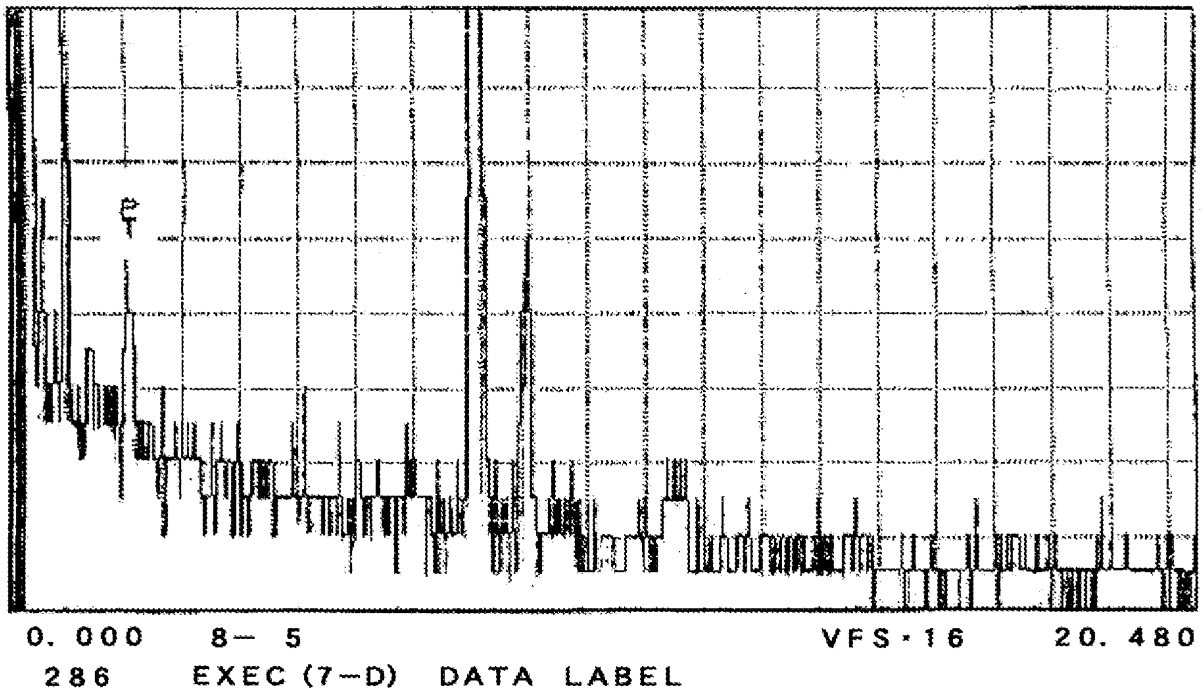
【Fig.6】



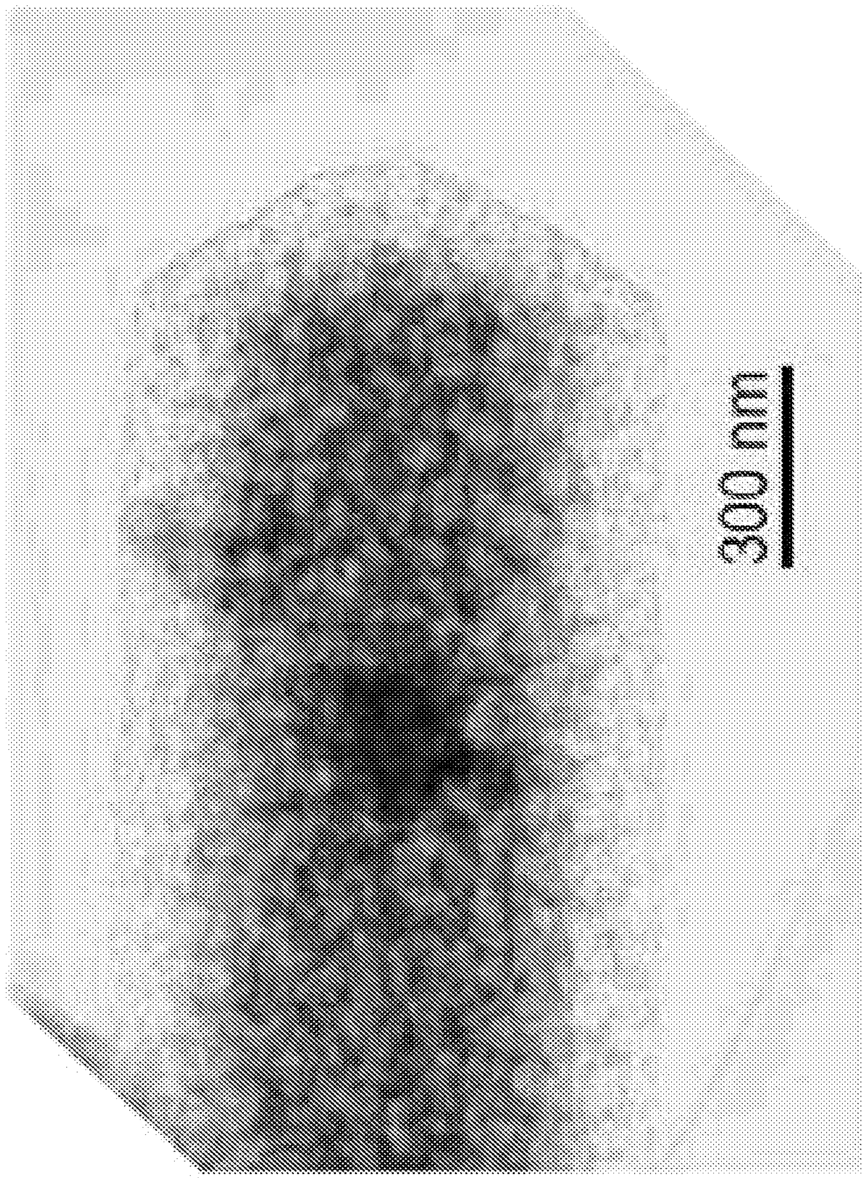
【Fig.7】



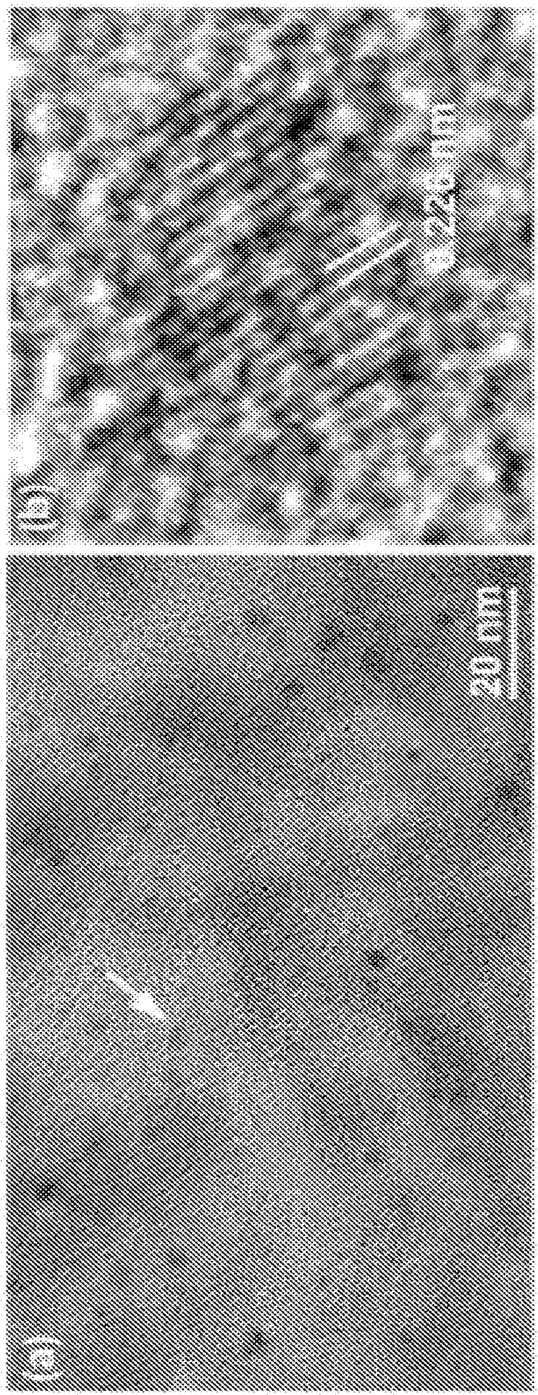
【Fig.8】



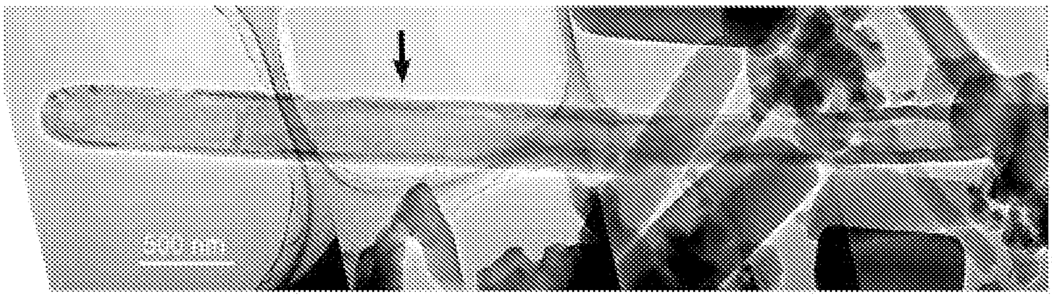
【Fig.9】



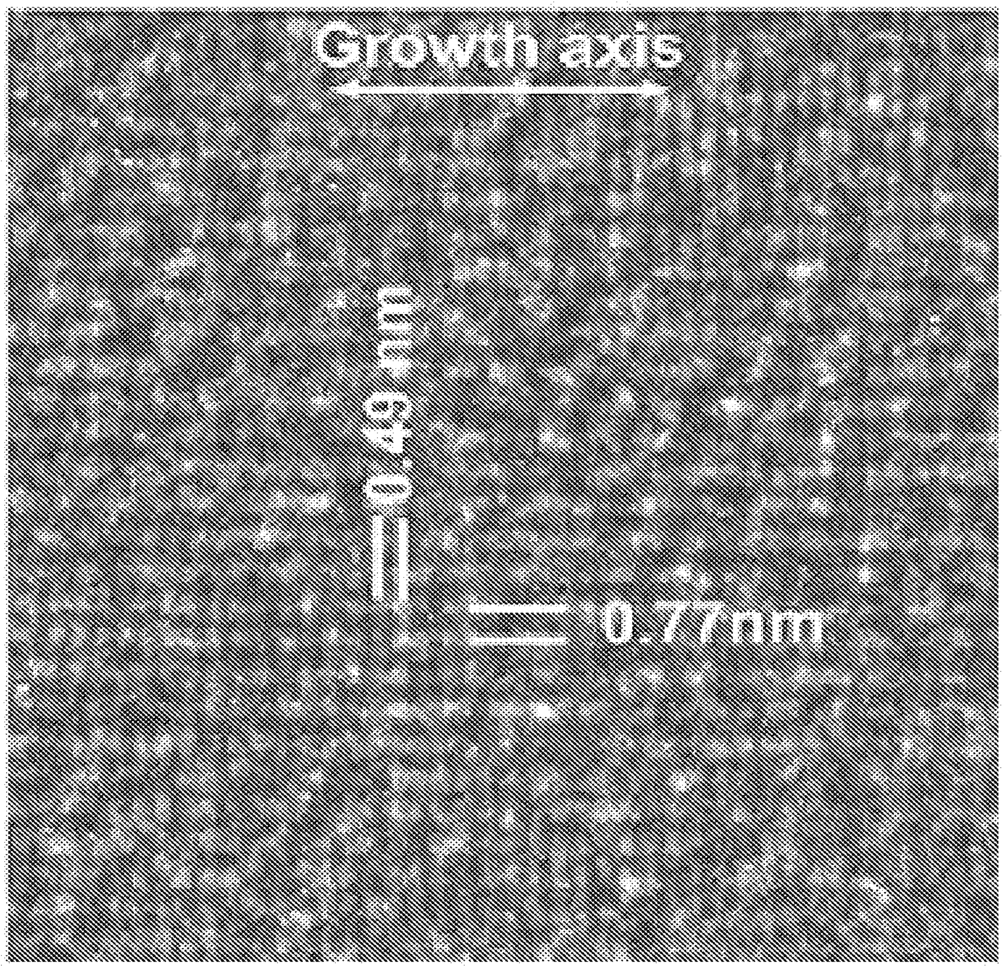
【Fig.10】



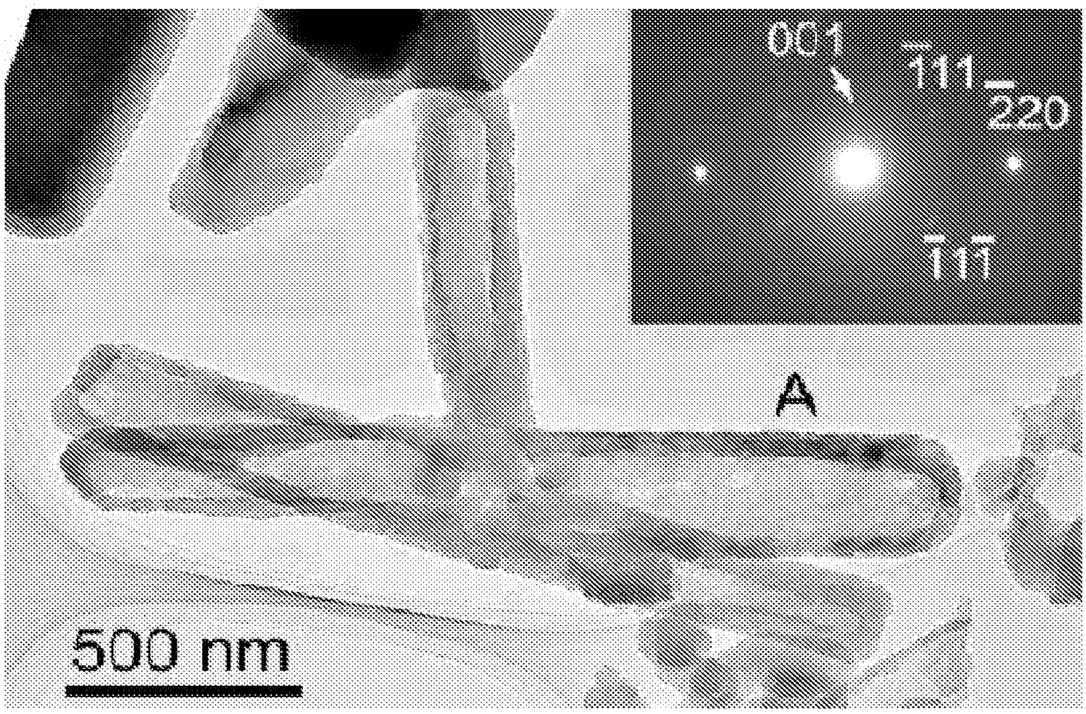
【Fig.11】



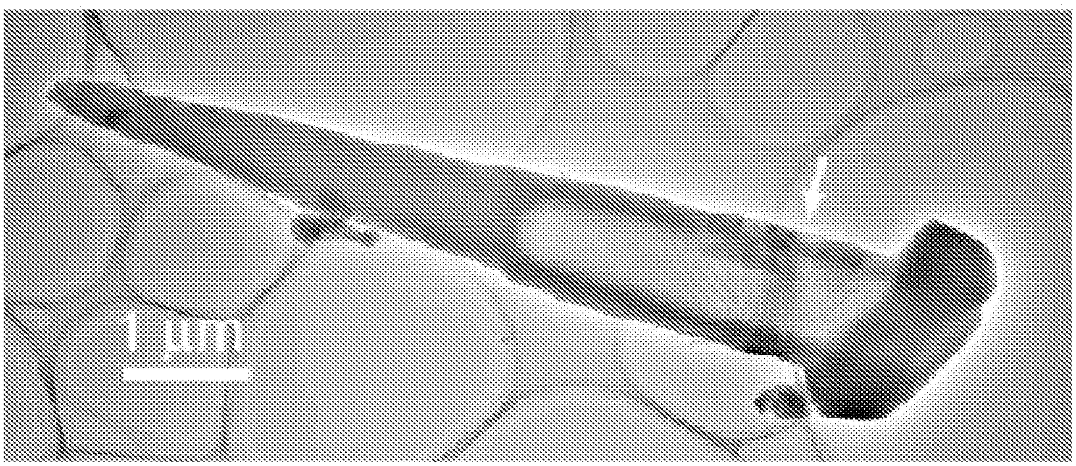
【Fig.12】



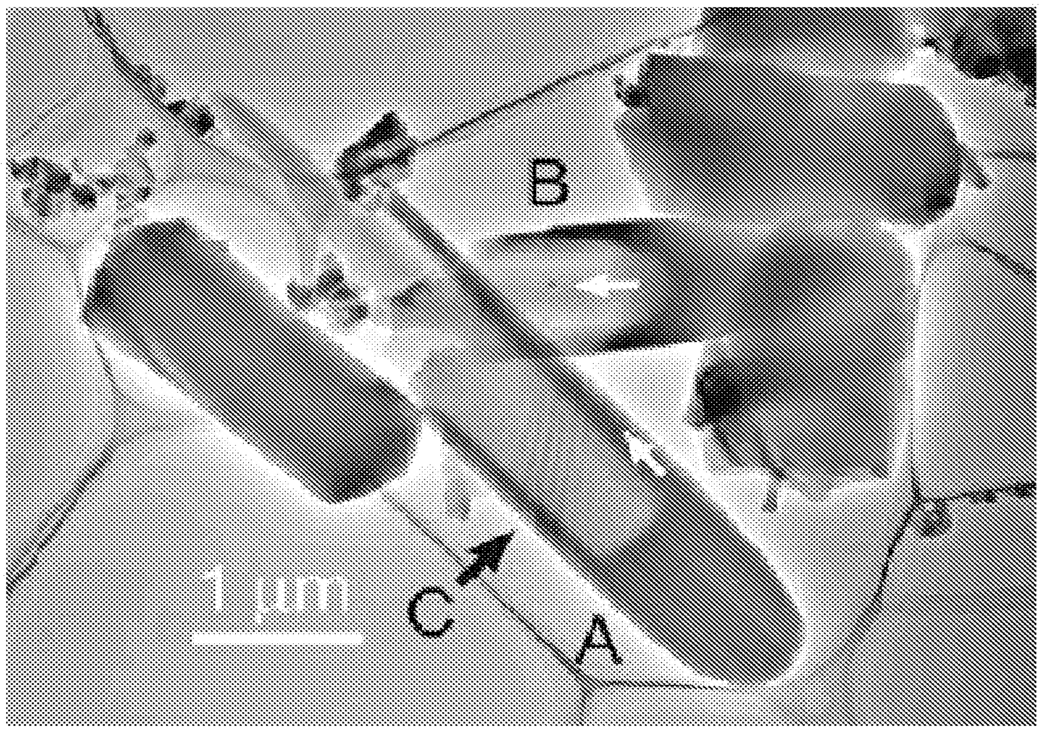
【Fig.13】



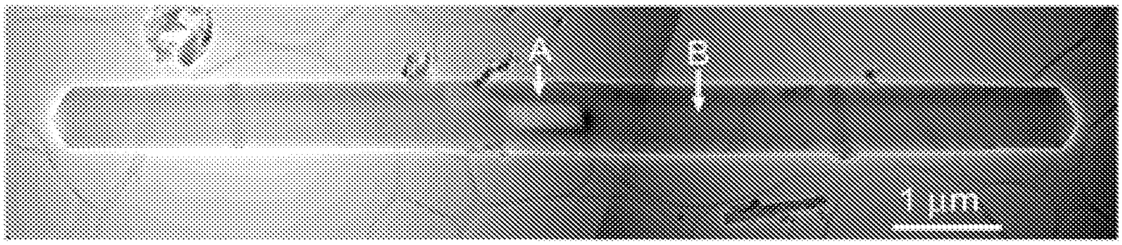
【Fig.14】



【Fig.15】



【Fig.16】



【Title of the document】Abstract

【Abstract】

【Problem】 The purpose of the invention is to provide fullerenes having a feature in the new shape.

【Means for resolution】 A needle crystal in the form of a capsule comprising fullerene molecules such as C_{60} and a C_{60} platinum derivative and having a hollow portion (a fullerene shell capsule) is provided. The fullerene shell capsule which has been prepared by the liquid-liquid interface precipitation method, which comprises (1) a step in which a solution containing a first solvent dissolving fullerene therein is combined with a second solvent in which the solubility of fullerene is lower than in the above first solvent; (2) a step in which a liquid-liquid interface is formed between the above solution and the above second solvent; and (3) a step in which a carbon fine wire is precipitated on the above liquid-liquid interface, has a novel characteristic in its form and can be used as a catalyst supporting material, a raw material for a plastic composite material, a storage material for gas such as hydrogen, a catalyst for fuel cell, or the like.

【Selected Figure】 Fig.2